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Sharp Cu@Sn nanocones on Cu foam for highly Selective and efficient electrochemical reduction of CO₂ to formate

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Electrochemical reduction of aqueous CO_2 into formate is subject to the poor selectivity and low current density with conventional Sn-based catalysts owing to the inert property of CO_2 molecule and the low amount of active sites. Recently, it is demonstrated that alkali metal cations could greatly enhance the selectivity for CO_2 reduction via stabilizing the key intermediates (M. Liu et al., *Nature* 2016, **537**, 382-386), which leads to an effective solution to this problem by concentrating local metal cations through tailoring the catalyst structure. Herein, we synthesized spiky Cu@Sn nanocones over macroporous Cu foam for this purpose, which has a curvature radius of 10 nm via facile electrochemical coating of a thin layer of tin over Cu nanoconic surface. The faradaic efficiency of 90.4% towards formate production is achieved, with a current density of 57.7 mA•cm² at -1.1 V vs. RHE, which far exceeds the results of the tin catalysts at the-state-of-art. The performance should be attributed to the combined effects of sharp conical feature that facilitates the enrichment of surface-adsorbed metal cations and the promotion of the mass transfer and active sites growth favored by the three-dimensional porous network.

Introduction

Electrochemical reduction of carbon dioxide offers a promising approach for its conversion into chemical fuels under ambient condition.¹⁻⁴ On the other hand, it can also be used for the storage of excessive and renewable electric energy, generated by the intermittent wind and solar power, and helps to reduce the greenhouse gas emission.⁵⁻⁷ Formate (or formic acid), one of the valuable liquid products from CO₂ electroreduction, is highly demanded as a promising carrier for hydrogen storage over others in terms of its relatively high capacity (52 g H₂/L) and low volatility (40 mmHg in vapor pressure at 20 °C).⁸⁻⁹ In addition, it can also serve as a heat transfer medium in the oil and gas field drilling, or as an important chemical feedstock in paper manufacturing,¹⁰ in synthesis of high-value aromatic compounds¹¹, or being directly used in fuel cells¹². Motivated by its considerable demands, many efforts in improving the

Conventionally, there are two strategies to enhance the electrocatalytic performance of heterogeneous catalysts on CO_2 conversion¹³: (1) increasing the intrinsic activity of active sites,^{8,14-18} such as creating the reactive single-atom structure¹⁸ grain boundaries⁸ and edge sites¹⁷; (2) increasing the number of active sites through controlling the nanoparticle size¹⁹ or designing a three-dimensional porous structure to increase the active surface area²⁰⁻²¹. It should be noted that, in a recent work by Liu et al., it was discovered that CO₂ reduction can be facilitated by the surface-adsorbed metal cations, e.g., K⁺, which can strengthen the carbon-metal (C-M) bond by reducing C-M distance, and consequently stabilize the CO₂ reduction intermediates.²² Moreover, they claimed that the local concentration of metal cation could be dramatically increased due to the strong electric field induced by highcurvature structures.²²⁻²³ Thus, a highly selective catalyst for CO₂ electroreduction into formate may be obtained with a specifically designed high-curvature structure.^{3,22} Nevertheless, their work on fabricating the sharp noble-metal catalysts is only achieved with the aid of fragile carbon paper support, which will be limited in practical applications considering the poor mechanical strength and low physical flexibility of electrodes, in view of the rigorous condition in reactors.²⁰

Among the various earth-abundant metal candidates (Cu, Co, Sn, Bi, and their oxide-derived catalysts),^{2,24-26} tin-based catalysts are particularly attractive due to their low cost and easy surface modification to the promotion on CO_2 electroreduction, giving the formate faradaic efficiencies

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selectivity and current density for CO_2 electroreduction into formate have been an active research subject in recent years.

ARTICLE

above 80%.^{17,19} However, they only yield low current densities about 10 mA•cm⁻² at the potentials of maximum faradaic efficiency.^{8,16,17,19} Therefore, it is of great interest to further enhance the formate production ability of cheap tin-based catalysts.

We hypothesized that an attractive way to achieve this goal is the synthesis of an electrocatalyst having a sharp feature in a three-dimensional (3D) framework, which will enable to enrich local metal cations within the 3D porous structure, and the 3D porous structure on the other hand could provide a large number of active sites and excellent mass transfer capacity. Through a facile, duplicatable and affordable electrodeposition process, we cultivated the spiky copper@tin nanocones over the macroporous copper foam substrate, and achieved an excellent selectivity in formate with a performance superior to the results of the tin catalysts at thestate-of-art. And this strategy provides a simple and efficient way in design of effective and inexpensive metal catalysts with Cu nanocones as the template, which provides rich active sites and favorable mass transfer and local metal cation enrichment to favor CO₂ reduction.

Experimental section

Materials

Copper foil (99.98%, 0.5 mm thick) was from Alfa Aesar; potassium bicarbonate (KHCO₃, 99.99%), copper sulfate (CuSO₄·5H₂O, 99.8%), nickel sulfate (NiSO₄·6H₂O, 99.9%), sodium hypophosphite (NaH₂PO₂, 99.0%), sodium citrate (Na₃C₆H₅O₇·2H₂O, 99.0%), orthoboric acid (H₃BO₃, 99.5%), polyethylene glycol, sodium hydroxide (NaOH, 97%) and stannous sulfate (SnSO₄, 99.0%) were purchased from Macklin, and used without further purification. pH meter (FE28, Mettler Toledo), epoxy (sigma-Aldrich), Ag/AgCl electrode (CH instruments), SCE electrode (CH instruments), platinum gauze (Tianjin ida) and copper foam substrate (99.99%, 2 mm thick, JYS company) were directly used without modification. All the aqueous solutions were prepared with Hitech-Sciencetool water. The bulk pH of the electrolytes after CO₂ saturation was shown in Table S1 (Electronic supplementary information).

Fabrication of Cu nanocones on copper foil (Cu nanocones)

The copper foil was mechanically polished with sandpaper, and subsequently rinsed in 0.5 M sulphuric acid, acetone and deionized water with sonication, respectively, finally dried in N₂ atmosphere (ESI, Fig. S1). The Cu nanocones electrode was prepared using a modified method.²⁷ Typically, the cleaned copper foil was immersed into the electrochemical bath containing 0.03 M CuSO₄, 0.0024 M NiSO₄, 0.24 M NaH₂PO₂, 0.05 M Na₃C₆H₅O₇, 0.5 M H₃BO₃ and 6 g L⁻¹ polyethylene glycol, where pH was changed to be 8 using NaOH (denoted as standard bath A). All electrolysis experiments in this work were controlled by a CHI660E potentiostat (CH Instruments). Electrodeposition was carried out at the potential of -1.08V (aqueous KCI-saturated Ag/AgCI) at 75 °C for 20 min with Pt mesh as counter electrode, during which the bath was

continuously stirred at a speed of 110 rpm. Then the prepared Cu-Ni nanocones electrode was washed with copious of deionized water and dried under vacuum overnight. Finally, the Cu nanocones catalyst was obtained by immersing Cu-Ni nanocones into 0.1 M H_2SO_4 for an hour to dealloy the nickel.

Fabrication of Cu@Sn nanocones on copper foil (Cu@Sn nanocones)

The Cu nanocones on copper foil was covered by chemically resistant epoxy with a surface area about 0.6 cm² exposed to the Sn electroplating bath, which consisted of 2 M NaOH, 0.1 M Na₃C₆H₅O₇, 0.05 M SnSO₄ (denoted as standard bath B). The electrodeposition of Sn on Cu nanocones surface were conducted at a constant current density of 3.3 mA cm⁻² with time of 200 s, 700s, 800 s, 900 s and 1400 s, respectively,²⁸ during which the solution was vigorously stirred. The resulting Cu@Sn nanocones were rinsed with deionized water and dried under vacuum overnight.

Fabrication of bulk Sn on copper foil (bulk Sn)

The bulk Sn electrode was prepared by electrodepositing nanostructured Sn on the cleaned Cu foil (0.6 cm² geometrical area) in standard bath B with vigorous stirring. The current density was kept constant at 3.3 mA cm^{-2} and the deposition time was set to 800s.

Fabrication of Cu@Sn nanocones on copper foam (Cu@Sn nanocones/Cu foam)

Electrodeposition of Cu-Ni bimetallic nanocones over Cu foam was performed in standard bath A at -1.12 V (aqueous KClsaturated Ag/AgCl) and 75 $^{\circ}$ C for 20 min, similar to the procedure of growing Cu-Ni nanocones on Cu foil, followed by the removal of nickel in 0.1 M H₂SO₄. Then the Sn electroplating was applied in standard bath B with a current density of 3.3 mA cm⁻² to obtain Cu@Sn nanocones/Cu foam, while the plating time was prolonged to 2100 s because of the increased deposition current density of Cu-Ni nanocones on Cu foam (ESI, Fig. S2 and S3).

Physical characterization

X-ray Diffraction (XRD) data were obtained with a Bruker D8 ADVANCE diffractometer using Cu-K α radiation (λ =0.15406 nm). X-ray photoelectron spectroscopy (XPS) was measured on an AXIS UltraDLD instrument with AI K α radiation (450 W). Field emission scanning electron microscopy (FESEM, JEOL JSM-7800F Prime) and Energy dispersive spectrum (EDS, Scientific NORANTM System 7) were used to observed the morphology and identify the elemental distribution of the samples. Scanning transmission electron microscopy (STEM) elemental mapping was taken on FEI TALOS F200X apparatus. ICP measurements were performed on an Agilent 725 Inductively Coupled Plasma Optical Emission Spectrometer.

Electrochemical measurements

An airtight two-compartment and the re-electrode H-cell was used for \mbox{CO}_2 electrolysis under ambient condition (ESI, Fig.

Journal Name

S4).²⁹ The electrolytes were filled into both cathodic and anodic compartments, separated by a nafion 117 membrane (Dupont).^{30,31} A Saturated Calomel Electrode (SCE) and platinum gauze served as the reference electrode and counter electrode, respectively. The SCE electrode was stored in fresh KCI-saturated solution after electrolysis, and periodically checked against the pristine one to record the minute potential drift. All the reported potentials were corrected for the Ohmic loss (iR_u). The Ru values were measured using Ru test function built in the potentiostat and automatically compensated by workstation with a level of 80% during electrolysis, while the remaining 20% was corrected manually following the equation:^{29,32,33}

 $E_{100\%iR\text{-}corrected} = E_{80\%iR\text{-}corrected} - 20\% \times R_u \times average i$

Where $E_{100\% \ iR-corrected}$ is the final potential; $E_{80\% \ iR-corrected}$ is the applied potential in the electrolysis; average i is the average current obtained by dividing the total electric charge by the electrolysis time. In this work, the reported current density was normalized by the geometric surface area, and all potentials applied for CO₂ electrolysis were converted to the reversible hydrogen electrode (RHE) scale using:

 $E_{RHE} = E_{SCE} + 0.242 V + 0.0591 \times pH_{electrolyte}$

Prior to each run, the oxide on the catalyst surface was reduced at -1.2 V (vs. SCE) in N₂-saturated electrolyte for 10min, followed by bubbling CO₂ into electrolyte for 30min at 60.0 sccm. During the electrolysis, the cathodic electrolyte was continuously purged with CO₂ at 20.0 sccm and magnetically stirred at a fixed speed.

Product quantification

The quantification of gas products was performed with an online gas chromatograph (Synpec M3000). H₂, CO, CH₄ and CO₂, multi-carbon compounds were automatically separated using two different columns (a plot Q column and a plot U column), and subsequently quantified by thermal conductivity detectors (TCD). External standard method was used and calibrated with a standard gas mixture consisting of H₂, CO, CH₄, C₂H₄ and CO₂. The partial current densities of CO and H₂ production were calculated from the GC peak areas as follows:³⁴

$$j_{co} = \frac{\text{peak area}}{\alpha} \times \text{flowrate} \times \frac{2Fp_0}{RT} \times (\text{electrode area})^{-1}$$
$$j_{H_2} = \frac{\text{peak area}}{\beta} \times \text{flowrate} \times \frac{2Fp_0}{RT} \times (\text{electrode area})^{-1}$$

Where α and β are conversion factors for CO and H₂ respectively based on calibration of the gas chromatograph with standard samples, p₀ =1.013 bar and T₀ = 273.15 K.

Formate concentration was analyzed on a Bruker 600 MHz NMR spectrometer.³⁵ Standard curve was made using sodium formate (99.99%, Sigma-Aldrich), D_2O (99.9%, Sigma-Aldrich) and internal standard (Tris(trimethylsilyl) phosphate, TMSP, 0.05 wt% in D_2O , Sigma-Aldrich), shown in Fig. S5. A 0.3 mL catholyte after electrolysis was added to a mixture of 0.02 mL internal standard (0.05 wt% TMSP) and 0.18 mL D_2O . The 1D 1H spectrum was measured with water suppression using a presaturation method. The area ratio of the formate peak to the TMSP peak was compared to standard curve to quantify

the formate concentration, and the faradaic efficiency was calculated as follows:

Faradaic efficiency =
$$\frac{2F \times n_{formate}}{Q}$$

where F is the Faraday constant, $n_{formate}$ is the total amount of formate, Q is the total electric charge.

Numerical simulation

The free electron density on different electrodes was simulated using Electric Currents modules of COMSOL Multiphysics under a specific electrode bias potential according to the previous work.^{22,23} The radius of high-curvature sharp tip was set to be 10 nm and the bulk Sn particle was assumed to be spherical with a diameter of 500 nm. All 3D catalysts were represented by 2D axisymmetric models on the simulation, while the conductivity of tin-based electrode was set to be 8.8×10^6 S m^{-1.36} The electric field was the opposite gradient of the electric potential:

 $\vec{E} = -\nabla V.$

In this work, we used the Gouy-Chapman-Stern model which is composed of a Helmholtz layer and a diffusion layer to describe the electric double layer. The surface-adsorbed potassium ions in the Helmholtz layer was assumed to be monalayer. The diffusion layer was established based on the equilibrium between electrostatic force and diffusion. To calculate the cation density in the electrical double layer, the "Electrostatics" and the "Transport of diluted species" modules were combined and solved in the steady state:

$$\nabla^{2} V=0 \quad d < d_{H}$$

$$\nabla^{2} V=(C_{k}-C_{HCO_{3}})F \quad d > d_{H}$$

$$\nabla \cdot \left(D\nabla C_{i}+\frac{DZ_{i}}{k_{B}T}C_{i}\nabla V\right)=0$$

Where the d is the distance from electrode surface to the electrolyte, and the C_i are the concentration of potassium or bycarbonate, respectively. The thickness of the Helmholtz layer d_H, the valencies Z_i , the temperature T and the diffusion coefficient D were taken from prior work.²²

Results and discussion

Characterization of the as-synthesized catalysts.

As illustrated in Fig. 1a, the fabrication process of Cu@Sn nanocones started with the synthesis of Cu-Ni nanocones on the Cu foil. With the utilization of nickel mediator and H₃BO₃ crystal modifier in the electroplating bath, the vertical growth of copper-nickel nanocrystals can be accelerated by the deposited nickel atoms on the tip which was reduced by the hypophosphite and instantly displaced by the copper ions owing to their difference in redox potentials, while the lateral growth was simultaneously inhibited by a modifier, which eventually led to the formation of a highly dense bimetallic conical structure (ESI, Fig. S2, S6, S7 and S8).²⁷ Subsequently, the surface nickel (ESI, Fig. S7) of nanocones was removed from immersion in dilute sulphuric acid,^{37,38} followed by the electrodeposition of tin at a constant current density (ESI, Fig. S9),²⁸ and final nanoconic form of catalyst was generated.

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Fig. 1 (a) schematic illustration of the key steps in preparing Cu@Sn nanocones. (b) XRD patterns, (c) Sn 3d 5/2 XPS spectra of different catalysts.



Fig. 2 SEM images of (a), (b) Cu@Sn nanocones on Cu foil. (c) STEM elemental mapping of Cu@Sn nanocones. (d) STEM image of Cu@Sn nanocones. (e) TEM image of Cu@Sn nanocones. (e

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(e) TEM image	

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The crystal structure of Cu nanoconic precursor after removing nickel was investigated with XRD measurements (Fig. 1b), which shows a face-centered cubic (fcc) structure with (111), (200), (220) crystal facets (JCPDS 04-0836). X-ray photoelectron spectroscopy (XPS) analysis reveals that nickel peaks are absent after the dealloying process, indicating the complete removal of nickel atom from Cu nanoconic surface (ESI, Fig. S10). After electroplating of tin, four additional peaks located at 30.6°, 32.0°, 44.9° and 55.3° are observed in the XRD pattern of Cu@Sn nanocones (Fig. 1b), which are indexed to the (200), (101), (211) and (301) planes of metallic tin (JCPDS 86-2265), respectively. However, the detailed Sn 3d 5/2 XPS spectrum shows the co-existence of Sn⁴⁺ (486.5 eV) and Sn⁰ (484.6 eV) on the catalyst surface (Fig. 1c), due to the strong oxygen affinity to tin which makes it easy for the surface to be partially oxidized in the air.^{19,35}

The morphology and structure of the as-prepared samples were investigated by scanning electron microscopy (SEM). Fig. S11 reveals a layer of uniform and densely packed Cu nanocones with radius as small as 10 nm lying on the copper foil substrate, which have slightly rough surface. The Cu@Sn nanocones inherit the conical structure of the Cu nanoconic precursors and become smoother (Fig. 2a and 2b). In addition, scanning transmission electron microscopy equipped with energy dispersive X-ray spectroscopy (STEM-EDS) mapping images clearly show the uniform and conformal coating of Sn on Cu nanoconic surface (Fig. 2c). A further morphology examination of Cu@Sn nanocones using STEM confirms that the catalyst has a high-curvature conical structure, consistent with the SEM results (Fig. 2d). High-resolution TEM (HRTEM) image of a nanocone tip shows an ordered crystalline structure in the interior, and an approximate 3 nm thick mixture on the surface is identified (Fig. 2e). The inner lattice spacing is 0.213 nm, belonging to the (111) plane of fcc copper.²⁷ The outside layer verified by HRTEM tests was most likely composed of tetragonal Sn that showed the lattice fringes of (101) $planes^{17,39}$ and partially oxidized SnO_x^6 , which would be reduced to metallic Sn under cathodic potentials during CO₂ reduction.²⁰ Based on above structural characterizations, we believe that the dense Cu@Sn nanocones electrode consists of sharp tips with surface fully covered by a thin Sn/Sn oxides hybrid layer. Unexpectedly, a small amount of bulk Sn was also observed lying above the Cu@Sn nanocones layer after Sn deposition (ESI, Fig. S12). To highlight the catalytic performance of Cu@Sn nanocones for CO2 reduction, bulk Sn deposited on Cu foil was prepared (Fig. 2f and 2g).

Electrocatalytic Performance of CO₂ reduction

The CO₂ reduction ability of as-synthesized catalysts was first tested by performing cyclic voltammogram (CV) measurements in N₂ or CO₂-saturated 0.1 M KHCO₃ (ESI, Fig. S13). The cathodic current densities in N₂ atmosphere are due to the hydrogen evolution, among which the Cu nanocones had a most positive onset potential around -0.5 V. In addition, a lower current density was observed in CO₂ atmosphere for Cu nanocones relative to N₂ atmosphere, which may originate from the slight inhibition of adsorbed CO against the H₂

evolution.²¹ In contrast, Cu@Sn nanocones with Sn deposition time of 800 s and bulk Sn both displayed increased catalytic activities with CO_2 purge, while faster reduction kinetic was achieved on the former over the entire potential window. The cathode peaks around -0.2 V were attributed to the reduction of tin oxide on the catalyst surface,⁶ and not appeared on Cu nanocones electrode.

To investigate the catalytic performance of Cu nanocones, Cu@Sn nanocones (after optimizing the Sn deposition time, all Cu@Sn nanocones were referred to the Cu@Sn nanocones with Sn deposition time of 800 s hereafter, Fig. S14 and S15) and bulk Sn electrodes for CO₂ reduction, electrolysis at various potentials were conducted in 0.1 M CO2-saturated KHCO₃ electrolyte. The gaseous product and liquid product were determined using gas chromatography and nuclear magnetic resonance spectrometer, respectively. As expected, the total current densities of all samples gradually rose when applied potentials became more negative (Fig. 3a and Fig. S16). Notably, the formate faradaic efficiency of Cu@Sn nanocones increased rapidly at first as potential negatively shifted and also significantly exceeded that of bulk Sn over the entire potential range, achieving a maximum level of 88.4% at -1.1 V (vs. RHE) (Fig. 3b). The H₂ and CO accounted for the remaining products, and no other hydrocarbon was observed (Fig. 3c and Fig. 3d). After CO₂ electrolysis, the conical structure of Cu@Sn nanocones was well preserved (ESI, Fig. S17). For the bulk Sn deposited on Cu foil, the formate selectivity only has a moderate value of 64% at -1.1 V (Fig. 3b), close to the value of prior work.²⁵ Although Cu nanocones delivered the highest current densities from -0.6 V to -1.2 V, it primarily produced H_2 and displayed low formate faradaic efficiencies below 31% (Fig. S18). Meanwhile, a small amount of CH₄ and C₂H₄ were also detected in gas products (ESI, Fig. S18). For the prior Cu-Sn alloy catalysts, the bimetallic Cu-Sn interface (formed by depositing Sn on Cu surface) was directly exposed to the electrolytes and reagents. The presence of optimized amount of Sn on Cu surface could alter the adsorption of H and disfavor the hydrogenation process to reduce the selectivity towards H₂ and HCOOH, while keep the adsorption of CO relatively unperturbed on the Cu sites, resulting in the improved CO selectivity above 80%. 35,40,41 On the basis of CO₂ reduction results and TEM characterization, it can be concluded that the sharp nanostructured Sn fully coated on the Cu nanoconic surface, are the active sites responsible for the improved formate selectivity in CO₂ reduction rather than the Cu nanocones support or the bimetallic Cu-Sn interface. Moreover, the Cu@Sn nanocones displayed the highest formate partial current density (j_{HCOO}) at potentials negative than -0.8 V, and obtained a j_{HCOO} of 18 mA • cm⁻² at -1.1 V, which was roughly 2.1 and 2.9 times higher than that of bulk Sn and Cu nanocones, respectively (ESI, Fig. S19). According to the measured double-layer capacitance in Fig. S20, the electrochemical active surface area (ECSA) for Cu@Sn nanocones was 1.8 times higher than that of bulk Sn. Therefore, the 2.1 times increase in formate partial current density of Cu@Sn nanocones relative to bulk Sn would indicate a faster electron transfer and higher intrinsic activity. The





Fig. 1 (a) Total current density, (b) Formate faradaic efficiency, (c) H₂ faradaic efficiency, d) CO faradaic efficiency, e) Tafel plots of different Sn-based catalysts measured in CO₂saturated 0.1 M KHCO₃ at various potentials. f) Formate partial current density of Cu@Sn nanocones vs. concentration of HCO₃ at -0.9 V (vs. RHE).

onset formation^{2,29} of formate on sharp Cu@Sn nanocones can be obviously observed at -0.55 V, implying an overpotential of 540 mV (the equilibrium potential is -0.01 V vs. RHE), which is reduced by 100 mV compared to that of the bulk Sn (Fig. 3b), and this result further verifies the enhanced performance.

To explore the electrokinetic mechanism of CO_2 reduction on the Cu@Sn nanocones and bulk Sn, Tafel plots were constructed and presented in Fig. 3e. It is widely considered that the electroreduction of CO_2 to formate involves two electrons [equations (1)-(5)], which is initiated by the first electron transfer to a CO_2 molecule to form a surface adsorbed

 CO_2^{\bullet} intermediate, and followed by the reaction of CO_2^{\bullet} intermediate with one proton and another electron to generate the final product:^{16,20,42,43}

(4)

$CO_2(solution) \rightarrow CO_2 (ads)$	(1)	
$CO_2(ads) + e^- \rightarrow CO_2^{\bullet-}(ads)$	(2)	
$CO_{2}^{\bullet}(ads) + HCO_{2}^{\bullet} \rightarrow HCOO^{\bullet}(ads) + CO_{2}^{2-}$	(3)	

 $HCOO^{\cdot}(ads) + e^{-} \rightarrow HCOO^{-}(ads)$

 $HCOO^{-}(ads) \rightarrow HCOO^{-}(solution)$ (5) The Tafel slope of bulk Sn is 118.5 mV dec⁻¹, corresponding to a mechanism where the reaction rate is controlled by the initial electron transfer to the adsorbed CO₂ [equation (2)], while a

Tafel slope of 59 mV dec⁻¹ implies the rate-determine chemical step [equation (3)].⁴² Interestingly, Cu@Sn nanocones showed an intermediate slope of 80.1 mV dec⁻¹. To further explore the reaction mechanism, electrolysis were performed at constant potential at NaHCO₃ concentrations increasing from 0.025 M to 0.2 M,¹⁹ with NaClO₄ added into the low concentration samples to maintain the ionic strength (note that, the solubility of KClO₄ in the water is only 0.108 M at ambient condition, so the sodium-based electrolytes were used). The results in Fig. 3f reveals that formate partial current density is

independent on the HCO_3^- concentration, suggesting that the CO_2 reduction rate for Cu@Sn nanocones is determined by the

intermediate CO_2^{\bullet} formation [equation (2)] rather than the proton transfer from bicarbonate [equation (3)].^{42,43} Nevertheless, the smaller Tafel slope of Cu@Sn nanocones indicates a faster reaction kinetic for CO₂ conversion relative to

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bulk Sn,^{8,17} implying that reagent concentration might be favored.

To further understand the improved current efficiency towards formate on Cu@Sn nanocones, electric-field effect of nanocones was investigated via COMSOL Multiphysics simulation.^{22,23} As shown in Fig. 4a, charged spiky nanocones can increase free electron density on the surface and hence create a stronger electric field (arrows depicted in Fig. 4a). On the contrary, bulk Sn particles possessed only few electrons (Fig. 4b). Specifically, the metallic nanocone with radius of 10 nm could enhance the intensity of the electric field at the tip by a factor of 9 as compared with the bulk Sn and hence dramatically increase the concentration of adsorbed K^{*} at reactive sites by 12 times via field-induced-reagent-concentration (FIRC) effect (Fig. 4c and 4d).^{22,23} Moreover, DFT

calculations demonstrated that the adsorbed K⁺ could generate a high electric field with an absolute value of 1 V/Å in the vicinity of the metal cation, which is favorable to the adsorption of CO₂ and electron transfer to form the reaction intermediate CO_2^{\bullet} , leading to the improved formate faradaic efficiency.^{44,45} In addition, the concentrated K⁺ could make more CO₂ adsorbed on the surface sites and limit the active sites available to the proton reduction to H₂.^{46,47} To get a better insight into the effect of K⁺ concentration on CO₂ reduction, electrolysis was conducted on Cu@Sn nanocones and bulk Sn electrodes separately in KCl/KHCO₃ solutions of different concentrations at -1.1 V. The addition of KCl to the electrolyte would change the K⁺ concentration while keeps the bulk pH almost unchanged (Table S1). As shown in Fig. 4e, the



Fig. 4 Simulated free electron density distributions on the surface of (a) Cu@Sn nanocones and (b) bulk Sn are presented as a color map. Electric field distribution around the electrode is denoted by arrows where the size and direction of each arrow shows the intensity and direction of the field. Computed surface K^+ densities of (c) Cu@Sn nanocones and (d) bulk Sn. Effect of potassium concentration on CO₂ reduction at -1.1 V: (e) Formate faradaic efficiency and (f) H₂ faradaic efficiency.

Journal of Materials Chemistry A Accepted Manuscrip

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formate faradaic efficiency on Cu@Sn nanocones was continuously and gradually improved when the bulk K concentration was raised from 0.1 M to 0.4 M (not the influence of Cl⁻, Fig. S21), corresponding to the suppression of ${\rm H_2}$ evolution (Fig. 4f). Meanwhile, electrochemical impedance spectroscopy (EIS) was performed on Cu@Sn nanocones in CO₂-saturated electrolytes with various K⁺ concentration. Fig. S22 shows that charge transfer resistance (R_{rt}) was reduced with the increament of K^{+} concentration from 0.1 M to 0.4 M, suggesting an enhanced electron transfer to CO₂ for forming the $C0_2^{\bullet-}$ intermediate. Because of the FIRC effect, the local K^{\bullet} comcentration on the nanotip was high, so the effect of the increased potassium concentration in the bulk electrolyte on formate selectivity was relatively weak.²² The trend of the increment in formate selectivity with the increasing K^{+} concentration was more obvious on the bulk Sn. Neverthless, enriching local K^{+} ion on the catalyst surface by sharpening the structure with Cu@Sn nanocones is more effective than increasing the salinity in bulk electrolyte for catalyzing CO2 conversion to formate.

Practically, loading of catalyst on three-dimensional porous substrate such as copper foam (ESI, Fig. S23) could increase the active sites and facilitate the mass transfer of reactants to improve the catalytic activity for CO₂ conversion.^{20,23} Therefore, we facilely cultivated the Cu@Sn nanocones over Cu foam substrate via a facile electrodeposition process similar to the process on Cu foil (ESI, Fig. S24). SEM images reveal the densely packed Cu@Sn nanocones on the Cu foam framework (Fig. 5a), and the radius of the spiky tip is about 10nm (Fig. 5b). SEM-EDS mapping confirms the uniform and conformal coating of Sn on Cu nanocones (ESI, Fig. S25). Electrolysis at Cu@Sn nanocons/Cu foam was measured around the optimal potential (-1.0 V \sim -1.2 V) in CO₂-saturated solution consisting of 0.1 M KHCO₃ and 0.3 M KCl. Interestingly, Cu@Sn

nanocones/Cu foam reached a maximum formate faradaic efficiency of 90.4%, and delivered a high current density of 57.7 mA \cdot cm⁻² at -1.1 V (Fig. 5c), indicating a superior performance to most noble-metal-free Sn-based catalysts (Table S2). In addition to the high activity and selectivity, stability is another critical factor in evaluating the efficiency of a catalyst. The stability of Cu@Sn nanocones/foam catalyst was investigated at -1.1 V for 10 h in the optimal electrolyte with electrolyte being replaced every hour.^{6,26} As shown in Fig. 5d, we observed almost no decline of current density, and the slight fluctuation during electrolysis was ascribed to bubble formation and desorption on the catalyst surface. Meanwhile, the faradaic efficiency of formate was slightly decreased after a long-term test, but it was always above 82%. After 10 h electrolysis, the conical structure of Cu@Sn nanocones/Cu foam was maintained, but its surface became rougher (ESI, Fig. S26). This slight surface restructuring and sintering of nanostructured tin may expose Cu active sites during the electrolysis, which are more favorable to H₂ generation and may be responsible for the decreased selectivity in formate production.35,48

Conclusions

In summary, densely packed and spiky Cu@Sn nanocones electrodes were fabricated by a facile and cheap electrodeposition approach. As the high-curvature nanotip would generate a strong electric field to concentrate local K^+ , the as-prepared Cu@Sn nanocones on Cu foil was able to selectively reduce CO₂ to formate at a faradaic efficiency of 88.4%. Further combined with the large surface area and efficient mass transfer, the loading of sharp Cu@Sn nanocones



Fig. 5 (a), (b) SEM images of Cu@Sn nanocones/Cu foam. (c) Current density and formate faradaic efficiency, (d) stability test for catalysing CO₂ reduction at -1.1 V of Cu@Sn nanocones/Cu foam.

on three-dimensional copper foam gives an excellent catalytic performance with a faradaic efficiency of 90% and a high current density of 57.7 mA•cm⁻². The remarkable performance of highly dense and cost-effective Cu@Sn nanocones/Cu foam here may open up new avenues to design efficient electrocatalysts for the commercial formate production.

Conflicts of interest

There are no conflicts to declare.

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